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Danish Atomic Energy Commission

Research Establishment Risø

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Incorporation in Bitumen of Low-Level Radioactive Waste Water Evaporator Concentrate at the Danish Atomic Energy Commission Research Establishment Risø

by

Ib Larsen

Danish Atomic Energy Commission
Research Establishment Risø
Chemistry Department

Abstract

The plant for evaporation of radioactive waste water at the Research Establishment Risø has been in operation since 1959. The concentrate from this plant is stored as a semi-liquid, soluble sludge. Since November 1970 the concentrate has been incorporated in bitumen to form an insoluble solid. A description is given of the necessary laboratory experiments. The design principles for and experiences of operation with the finished bituminization plant are given.

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Introduction

At the Research Establishment Risø the radioactive waste water from reactors, laboratories, etc. is concentrated by evaporation [1]. The concentrate from this evaporation step contains about 180 grams of solids per litre. The solids have a composition which is relatively unique. The greater part of the soluble solids is sodiumsulphate, but the concentrate also contains chlorides, organic materials, and an insoluble sludge. It is composed of nearly all the chemicals used in the laboratories. Since the start of the research establishment this concentrate has been concentrated further in a final evaporator. Three different types of final evaporators have been tried. The concentrates from these all had the consistency of a thick, liquid sludge that is easily soluble. Several methods have been tried to make this sludge solid and insoluble, but all have been unsuccesful. Mixing with cement, for instance, was very difficult, and a very large volume increase could not be avoided, and as the concentrate has to be stored at Risø, the necessary space for storage would have to be increased by about a factor of six. To avoid this the semi-liquid sludge is stored in double drums with concrete between the drums. This solution is in the long run unsatisfactory.

In several countries sludge from the chemical treatment of radioactive waste water and to some extent also waste evaporator concentrates have succesfully been incorporated in bitumen, for instance in Belgium [2], France [3], and the United Kingdom [4]. In USA [5] experiments have been carried out, and in the Federal Republic of Germany at the Karlsruhe Research Establishment plans for incorporating evaporator concentrates in bitumen have been published [6]. In the light of this information we began in 1967 to think of using bitumen for incorporation of our radioactive waste concentrate. The special chemical composition of our waste concentrate, the minimal experience at that time with incorporation of evaporator concentrates in bitumen, and the comparatively small volume of our preconcentrate, which amounts to only about 15 m^3 a year, made it necessary for us to carry out our own experiments, as a plant made according to known principles would have been much too expensive for our purpose. We had, however, plenty of experiences with concentrating our preconcentrate by evaporation. We thought these experiences could be used, and our aim was to make the final concentration and incorporation in bitumen simultaneously to make the plant as simple as possible and to avoid the technical difficulties with the final evaporation step. The laboratory experiments were at the beginning not too succesful, but these difficulties have been overcome, and a bitumen plant has been installed instead of the previous final evaporator. Since November 1970 all our preconcentrate has succesfully been concentrated and incorporated in bitumen in this plant.

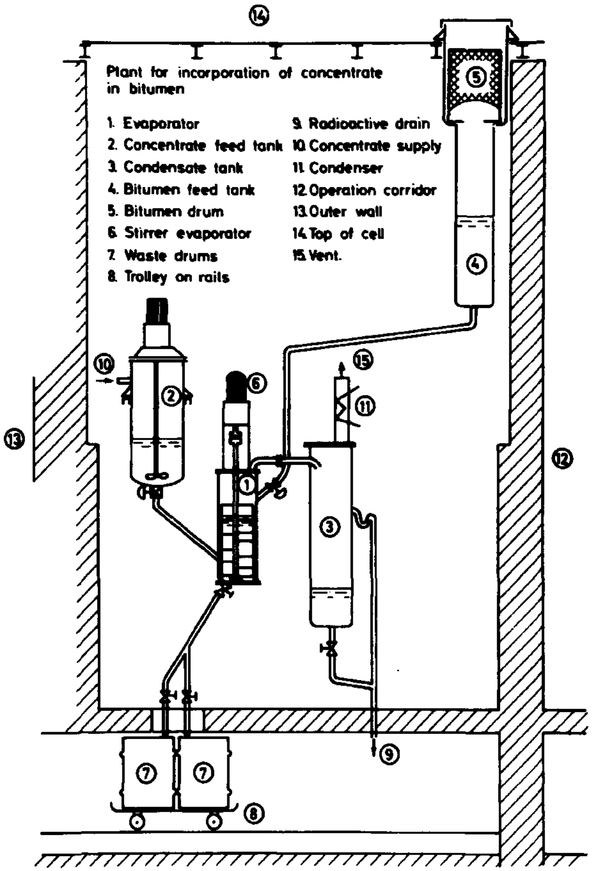
Laboratory Experiments

As the starting point for the laboratory experiments was used the batch process proposed by Blanco [5], where an emulsion of bitumen was employed as bitumen supply. In our experiments very good products were obtained by this procedure when pure salt solutions, which were to simulate our concentrate, were incorporated in bitumen. However, when we tried to incorporate our actual concentrate according to this method, the product was easily soluble in water. This was possibly due to the great content of organic chemicals in our concentrate, but we thought at the time that it was due to the very soft bitumen we were using. In our country bitumen emulsions are only produced from a very soft basic material. We tried therefore to produce an emulsion from a bitumen which was harder. It was quite a simple matter, but this emulsion was very unstable when it came into contact with the concentrate in the evaporator. We therefore decided to try to use molten bitumen still in the same apparatus. The molten bitumen was during constant stirring added to the evaporator, which had in advance been filled with some concentrate. In this way we obtained a suspension of the molten bitumen in the concentrate. When the water was then evaporated and the temperature was raised to 160°C, it was possible to draw off the product. It appeared, however, that also this product was comparatively easily soluble in water. Accidentally we found that if it was first heated to 200°C and then allowed to cool to 160°C before being drawn off, a very fine and leach-resistant product was obtained. This was probably a result of some of the organic chemicals being destroyed at 200°C. The organic materials, most of which are detergents, probably cause an increased solubility of the finished product.

We experimented with bitumen of three different hardness classes, penetration 10/20, 40/50, and 80/100. It appeared that the two hardest of these, 10/20 and 40/50, had about the same values with respect to solubility of the finished product. We chose to continue the further experiments with the softer of them, 40/50, as the technological problems could hereby be solved in the simplest way. This applies particularly to the following circumstances. At the time of feeding the temperature of the molten bitumen

should preferably not be very much higher than 100°C as there would otherwise be a risk of violent parboiling. When most of the water in the concentrate has been evaporated the temperature is around 110°C; a too hard bitumen will be very viscous at this temperature and demand an over-dimensioned stirrer. The draw-off may also give problems with a harder bitumen.

The results from these laboratory experiments were tested in an experimental plant with a volume of 10 litres and with an evaporation capacity of about one litre per hour. The experiences gained were used in the design of the real-size plant which is now used.



Bitumen Plant

The radioactive concentrate is now incorporated in bitumen in the plant shown in fig. 1. The main components are the bitumen feed tank, the concentrate feed tank, the evaporator, and the condensate tank (fig. 2).

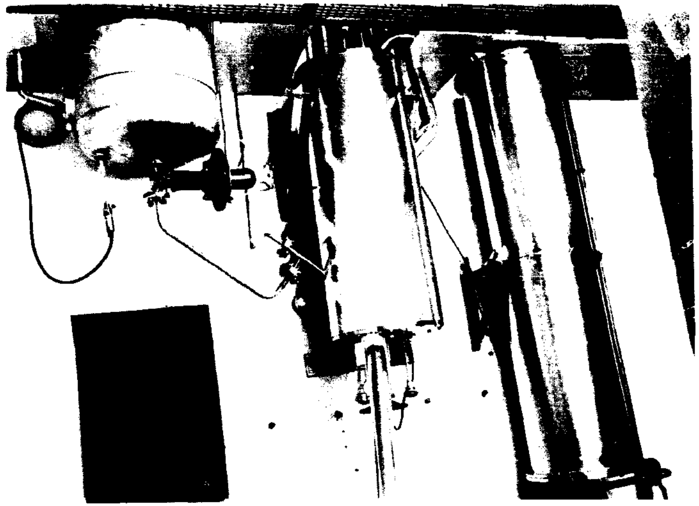


Fig. 2. From the left: concentrate feed tank, evaporator, and condensate tank.

The concentrate feed tank with a volume of 300 litres is for every batch supplied with 200 litres of concentrate from a concentrate storage tank through an air-operated valve. To preheat the concentrate the concentrate feed tank is equipped with an external electrical heating element with an effect of 3 kW.

The bitumen feed tank is supplied with bitumen directly from drums by placing the drums with the opening downwards in the top of the tank. Emptying a drum takes about fifty hours when bitumen with penetration 40/50 is used. The bitumen feed tank is heated by a thermostat-regulated electrical heating element with an effect of 3 kW. The temperature of the bitumen is kept at about 110°C. The bitumen is transported to the evaporator through an electrically heated pipe and an air-operated valve (fig. 3).

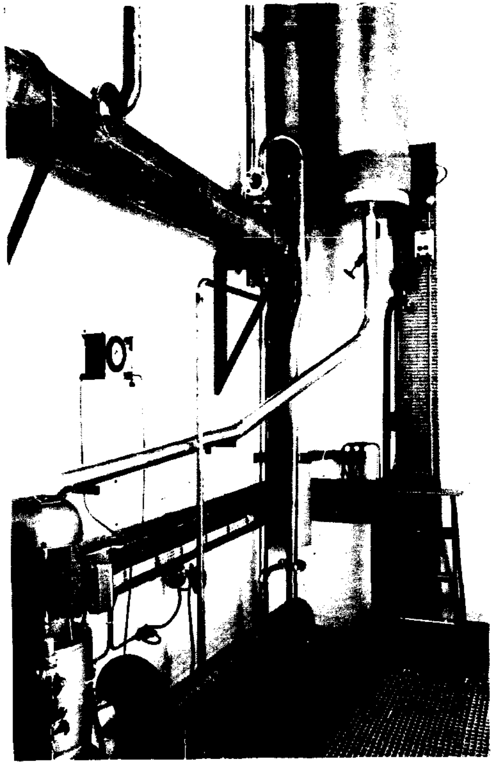


Fig. 3. In the background the bitumen feed tank with heating element, from the bottom of this the electrically heated bitumen feed pipe.

The evaporator is a cylinder which is heated externally by means of three electrical heating elements, each with an effect of 3 kW. The heating surface is from the inside of the cylinder swept by a slow-moving stirrer. This stirrer has at the bottom of the evaporator a steadying bearing made from bronze. This bearing may be replaced from the outside. At the top of the

evaporator the stirrer has a stuffing box and a powerful roller bearing. The stirrer is driven by a 4 kW electrical motor running at 60 revolutions per minute.

In the bottom flange of the evaporator there is besides the mentioned bearing, two resistance thermometers and the draw-off valve. This is a specially designed piston valve, where, when the valve is closed, the piston reaches into the evaporator. When the valve is open there is an entirely free passage through it. The product runs from this valve through an electrically heated pipe and through a special distrihution valve (fig. 4) down into one of

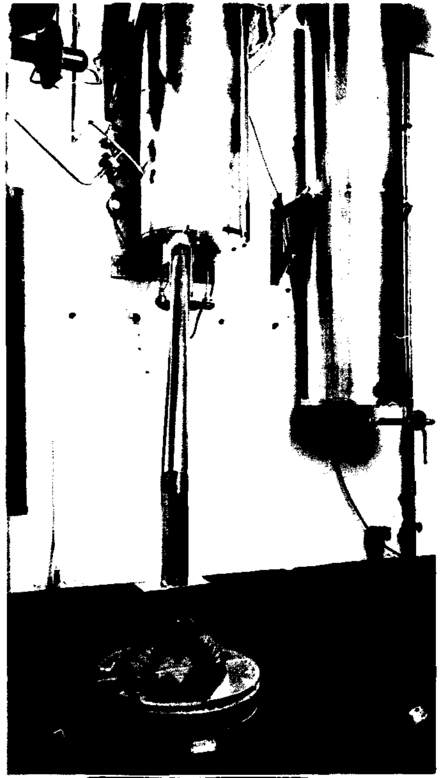


Fig. 4. In the foreground the distribution valve.

the two waste drums which are placed on a trolley in the basement under the bitumen plant (fig. 5).

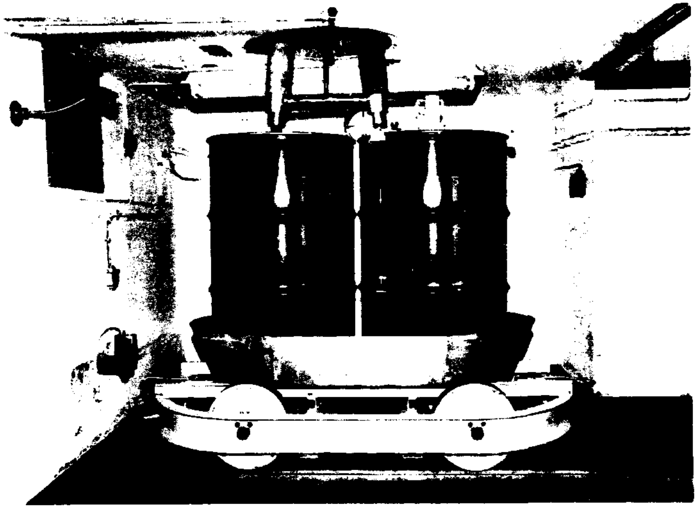


Fig. 5. The trolley with waste drums in the basement under the bitumen plant.

In the top flange of the evaporator there is as mentioned a stuffing box and suspension for the stirrer (fig. 6). Besides this there is a resistance thermometer, a 75 mm pipe for escape of the vapour, and a feed pipe for supplying anti-foam agent. A silicone anti-foam agent is used. Whether this is necessary we do not really know. In the laboratory experiments it was, however, necessary, and we preferred to continue this practice. The same feed pipe is used for admixture of ion exchange resins when we want to incorporate these in the bitumen.

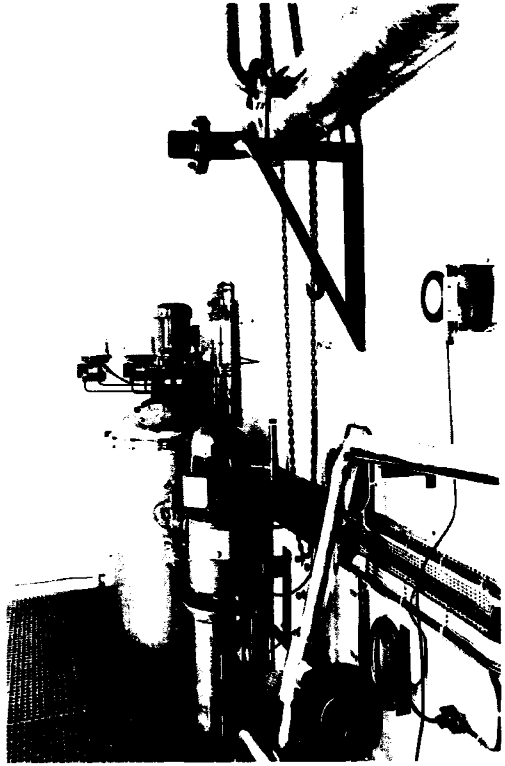


Fig. 6. In the foreground the stirrer motor of the evaporator placed on its top. In the background the concentrate feed tank.

On the one side of the cylinder (see fig. 2) between the lowest and the middle heating elements is placed a tube which is used partly for the feeding of concentrate and partly as bubbling tube for the liquid level measurement. We found it suitable to combine the two functions in one tube. Thus we succeed in keeping the bubbling tube free from residues due to drying and the concentrate feed pipe free from bitumen. The regulation of the liquid level is, however, impeded by this arrangement as the liquid level measurement is influenced when concentrate is supplied. This problem is solved by a time automatics that control the air-operated concentrate feed valve, which is of the diaphragm type. On the other side of the cylinder of the evaporator the bitumen feed pipe is placed. It is above the liquid level in the evaporator and above the heating elements.

The condensate tank is designed according to our experiences from the experimental plant. Here we had two cases where the bitumen boiled over into the condenser. Both times it happened during the bitumen feeding and was probably due to a too high bitumen temperature. As overboiling is, however, not quite out of question and as the cleaning work in such a case is very inconvenient, we took this into account at the designing of the condensate tank. The pipe for escape of vapour from the evaporator is a 75 mm pipe which runs directly into the condensate tank. The condenser is a tube helix placed in the condensate tank. This tank is constructed with a flanged bottom so that if overboiling happens, the bitumen will go straight to the tank without having to pass the condenser,and the bitumen may be removed through the bottom flange. Overboiling has luckily not taken place, and we do not expect it will as everything is better controlled in the actual plant than it was in the experimental one.

The condensate tank is emptied into the radioactive drain system, from where the water goes to the waste water evaporator for additional decontamination. The decontamination factor for the bitumen evaporator is 10.000. It has been unneccessary to clean further the vent gases from the condensate tank.

A batch process is started by the filling of about 200 litres of concentrate into the concentrate feed tank and starting the heating of this and the evaporator. The stirrer in the evaporator is started. About 50 litres of concentrate is transferred to the evaporator. Anti-foam agent is added. About 45 kg of bitumen is fed to the evaporator under steady stirring in about one hour. The temperature of the bitumen is about 110^{o}C. When the bitumen has been added, further amounts of concentrate are fed to the evaporator until the liquid level wanted has been reached. Evaporation of the water at or rate of about 10 litres per hour now begins. Concentrate is added at suitable intervals to keep a constant liquid level. When the concentrate feed tank is empty the addition of concentrate is stopped, while water still is evaporating, now with a falling liquid level in the evaporator. When most of the water has been evaporated, the temperature in the evaporator rises above the 105-110^{o}C of the evaporation period. The temperature is allowed to rise to 200^{o}C, while at the same time the temperature of the heating

elements is kept below 300^{o}C. The temperature in the liquid is kept at 200^{o}C for about 3 hours; the heating elements are then switched off, and the heating element on the drawing-off tube is turned on. When the temperature of the liquid in the evaporator has decreased to 170-180^{o}C, the liquid is filled into the waste drums. A batch process like this takes about 24 hours. At Risø it is possible to treat 4 batches a week.

The finished product contains about 36 kg of salts etc. from the concentrate mixed into about 45 kg of bitumen. The product thus has a solids content of about 45%.

Liquid level and temperature in all tanks are measured (fig. 7). The

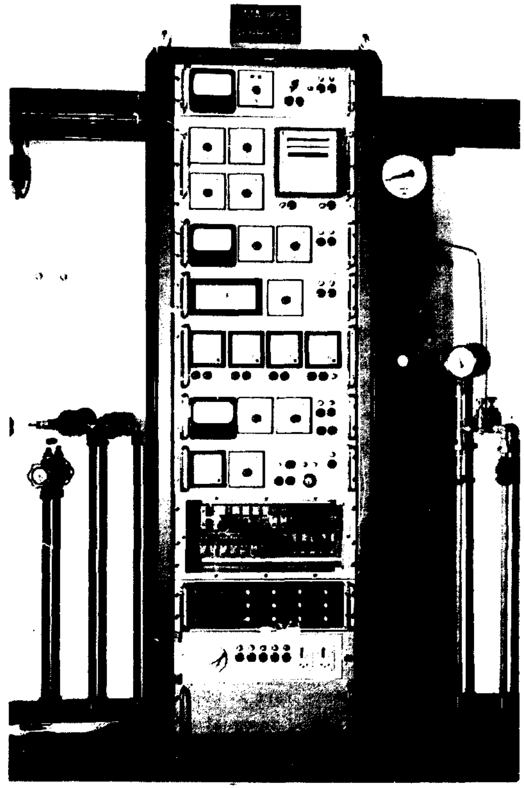


Fig. 7. Instrumentation panel for the bitumen plant.

most important of these measurements, liquid level in the evaporator and in the concentrate feed tank and the temperature in the evaporator, are recorded. The liquid level measurement in the evaporator regulates the feed of bitumen and concentrate to different levels and switches off the heating elements as the liquid level decreses. Apart from this the current consumption of the different heating elements and the stirrer motor is measured. The last-mentioned measurement controls the whole plant, as it is impossible to run the plant when the stirrer motor is standing still. All regulations are with on - off controls.

If we want to incorporate ion exchange resins into the bitumen, these are added by sluicing with water simultaneously with the addition of anti-foam agent. 20-30 litres of ion exchange resins per batch can without any difficulty be incorporated together with the radioactive concentrate.

The bitumen-concentrate mixture is not filled into empty waste drums, but is used for encapsulation of other radioactive wastes. In drums metallic waste is poured over directly with the bitumen product. That part of the product which cannot be used in this way, is poured into the space between the walls of double drums, which are used for compaction of solid compressible radioactive wastes.

From November 1970 until October 1972 the plant has treated about 130 batches, of which 18 were with simultaneous incorporation of ion exchange resins and concentrate. Altogether 26 m^3 of waste concentrate have been incorporated in bitumen. The experiences from these operations were quite satisfactory. All batches were run according to previously arranged programmes. The only trouble we had was with the concentrate feed valve. This valve (and the pipe between the concentrate feed tank and the evaporator) was a couple of times plugged with a heavy sludge, always at the moment when the first volume of concentrate was to be filled into the evaporator. Our preconcentrate is very dirty and contains much sludge, part of which resembles fine sand. We may replace this diaphragm valve with a ball valve, or perhaps make an arrangement to flush the valve and the feed pipe with water. It has during this period not been neccessary to clean any of the tanks in the plant. The interior of the evaporator is covered with a thin layer of bitumen, whereas the condensate tank is quite clean.

The only accident we have had occurred on a very busy day. We emptied the evaporator when the contents were at 200°C without waiting for the temperature to decrease to 170-180°C as usual and used the product to fill a drum. When half an hour later we looked into the drum again the contents in the drum were flowing over the edge into the saucer in which the drums

are placed (fig. 5). Apparently there is an evolution of gas at 200°C, and this continued after the product had been emptied into the drum, and the viscous product was rising. It was troublesome to clean the saucer and the outside of the drum, and after this accident we shall always take the time to run the plant in the proper way.

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